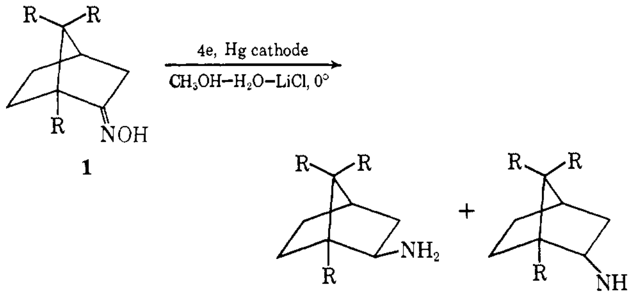
Stereoselective Electrochemical Reductions of Camphor Oxime and Norcamphor Oxime

Sir:

Despite increasing interest in synthetic organic electrochemistry,[1–3] little is known concerning the stereochemistry obtained in organic electrochemical reactions.[4] A working hypothesis has been advanced[4b] that, at least in reductions of alkyl halides, the electrode reactions resemble those in dissolving metal reductions.[5] We now report that (a) electrochemical reductions of camphor oxime (**1a**) and norcamphor oxime (**1b**) at a mercury cathode proceed with a high degree of stereoselectivity, and that (b) the products are in fact of *opposite* stereochemistry to those formed in dissolving metal (sodium–alcohol) reductions of **1a** and **1b** (Table I).



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2a, 99%
b, 0%

3a, 1%
b, 100%

a, R = CH_3; **b**, R = H

Table I. Stereochemistry in Reductions of Bicyclic Oximes[a]

Substrate	Reducing agent	Relative % products *exo*-Amine	 *endo*-Amine
1a	Mercury cathode	99	1
1a	$LiAlH_4$	99	1
1a	Na-EtOH	4	96
1b	Mercury cathode	0	100
1b	$LiAlH_4$	0	100
1b	Na-EtOH[b]	75	25

[a] Analyses by vpc on a 4-ft column packed with 8% Dowfax 9N9 on Fluoropak 80 at 130° and 180°. [b] K. Alder, G. Stein, and H. Rickert, *Ann.*, **525**, 221 (1936), suggested, from melting behavior of the hydrochlorides, that this reaction gives a mixture predominating in the *endo*-amine. That this is not so is shown by the identity of the major product with a known sample of *exo*-amine prepared by the method of H. C. Brown, W. R. Heydkamp, E. Breuer, and W. S. Murphy, *J. Am. Chem. Soc.*, **86**, 3565 (1964).

The preponderance in these electrolyses of the *less stable* of each epimeric pair of amines imposes stringent stereochemical requirements on the nature of the processes occurring at the electrode. Specifically, no conformationally mobile intermediates can be involved. In view of the similarity between the lithium aluminum hydride and electrochemical reductions, we suggest that the electrolyses proceed by kinetically controlled attack by the electrode upon each oxime from the less hindered side (*endo* attack on **1a** and *exo* attack on **1b**), very possibly with formation of an alkylmercuric species at the electrode surface,[6] followed by protonolysis with retention of configuration, by analogy to a number of other electrophilic aliphatic substitutions.[7]

Electrolyses were carried out at a mercury pool cathode in a divided cell of conventional design.[8] The anolyte was a 1 *M* solution of lithium chloride in 75% methanol–20% water–5% hydrazine; the catholyte was a solution of 2.0–3.0 g of the oxime dissolved in 100 ml of a 1 *M* solution of lithium chloride in 80% methanol–20% water;[9] both controlled-potential[10] reductions (−2.0 v *vs.* Ag-AgCl reference)[11] and constant-current electrolyses were carried out, at initial currents in the range 0.3–0.5 amp, with identical results. Yields of amines were in the range 50–70%; they were accompanied by small amounts of unreacted oxime and ketone formed by hydrolysis of the oxime.

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(1) A. F. Vellturo and G. W. Griffin, *J. Am. Chem. Soc.*, **87**, 3021 (1965).

(2) B. Belleau and N. L. Weinberg, *ibid.*, **85**, 2525 (1963).

(3) J. P. Petrovich, J. D. Anderson, and M. M. Baizer, *J. Org. Chem.*, **31**, 3897 (1966).

(4) However, see (a) R. Annino, R. E. Erickson, J. Michalovic, and B. McKay, *J. Am. Chem. Soc*, **88**, 4424 (1966); (b) C. K. Mann, J. L. Webb, and H. M. Walborsky, *Tetrahedron Letters*, 2249 (1966).

(5) See also J. H. Brewster, *J. Am. Chem. Soc.*, **76**, 6361 (1954).

(6) M. D. Morris, P. S. McKinney, and E. C. Woodbury, *J. Electroanal. Chem.*, 10, 85 (1965).

(7) *E.g.*, F. R. Jensen and K. L. Nakamaye, *J. Am. Chem. Soc.*, **88**, 3437 (1966).

(8) L. Meites in "Technique of Organic Chemistry," Vol. 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 3300.

(9) A referee has suggested that the sodium–alcohol reductions proceed by initial base-catalyzed formation of the equilibrium mixtures of epimeric 2-nitrosobornanes and norbornanes, that the composition of this mixture determines the *exo*:*endo* ratio of amines in the product, and that this epimerization pathway is not available in the electrolysis media. In fact, the solutions become quite basic during electrolysis, due both to accompanying solvent discharge[11] and to protonation of intermediates in the oxime reduction, so that the differences in product ratios cannot be due simply to basicity differences.

(10) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958.

(11) At this potential about 20% of the electrolysis current was involved in solvent discharge at the cathode; coulometry was not carried out, but there is in the literature a considerable amount of coulometric evidence that reductions of oximes indeed consume four electrons/molecule, *e.g.*, H. Lund, *Acta Chem. Scand.*, 13, 249 (1959).

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The Preparation and Configuration of the $[Re_4(CO)_{16}]^{2-}$ Anion. A Planar, Triangulated, Rhenium Carbonyl Cluster[1]

Sir:

In tetrahydrofuran, the reduction of $Re_2(CO)_{10}$ with sodium amalgam at room temperature yields[2] the pale yellow salt $Na^+Re(CO)_5^-\cdot 0.5C_4H_8O$. At reflux temperatures, or with other reducing agents such as sodium borohydride,[3] carbon monoxide is evolved and the solution acquires the intense red coloration typical of polynuclear carbonyl metallates.[4]

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(2) W. Beck, W. Hieber, and G. Braun, *Z. Anorg. Chem.*, **308**, 24 (1961).

(3) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).

(4) See $HFe_3(CO)_{11}$ [J. R. Case, and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960)] or $Ni_4(CO)_9{}^{2-}$ [cited in the review article by W. Hieber, *Angew. Chem.*, **72**, 795 (1960); *Angew. Chem. Intern. Ed. Engl.*, **72**, 65 (1961)] or, more recently, $Co_6(CO)_{14}{}^{4-}$ [P. Chini, *Chem. Commun.*, 440 (1967)].